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ATMOSPHERIC MEASUREMENTS OF NATURAL HYDROCARBONS
USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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SUMMARY

Recent field and modelling studies in the US and Europe have
demonstrated that the biogenic non-methane hydrocarbons such as
isoprene and the mono-terpenes can have a significant impact on
atmospheric formation of various oxidants and acidic compounds in
forested rural areas. At present, no comparable data exist on these
natural hydrocarbons in a Canadian setting. To obtain an annual data
set for a number of key volatile organic compounds (VOC) mainly of
natural origin, a 3-year project has been initiated starting from the
development and validation of analytical methods. High resolution gas
chromatography -mass spectrometry in combination with various sample
collection and preconcentration methods is in common use for analysis
of these natural VOC. A critical performance evaluation of the two
most widely employed sample-handling methods, i.e. (1) cryogenic
collection - preconcentration and (2) adsorptive sampling - thermal
desorption, is underway as a prerequisite for field measurements.
During the summer of 1988, samples collected at the Ministry's site at
Dorset and other forested areas have been examined using the cryogenic
preconcentration - GC method. Also, to enhance the quality and speed
of data acquisition, a fully automated preconcentration - injection
system is being developed as a reference sample handling device.

Introduction

Large quantities of non-methane hydrocarbons (NMHCs) are emitted into the atmosphere from vegetation. A recent emission inventory in Ontario indicates that the ratio of natural to anthropogenic NMHCs exceeds a factor of 20.[1,2] The natural NMHCs such as isoprene and mono-terpenes can play an important role in the atmospheric transforamtion of NO_x and SO_2, and in the formation of various oxidants, e.g. ozone, hydrogen peroxide, peroxyacetyl nitrate (PAN) and oxygenated organic compounds which contribute to regional-scale air pollution.[3,4] However, the ambient concentrations of natural NMHCs are presently unknown in a Canadian setting. High resolution GC/MS in combination with various sampling methods is widely employed for atmospheric measurements of NMHCs. However, there is a lack of well-established analytical protocols for these labile organic compounds at sub-ppb mixing ratio ($\leq 10^{10}$ molecule cm^{-3}). Thus, the initial phase of this project is devoted to a critical evaluation and improvement of sample-handling methods for GC/MS analysis.

Experimental

Figure 1 illustrates a schematic of sample handling system for GC/MS analysis. A sample preconcentration system consisting of a "cryogenic" absorption/thermal desorption-injection unit and vacuum gas-handling system constructed of stainless steel throughout have been assembled in-house. Details of the design and operation of this system are described elsewhere.[6] Also, a commercial "sorbent" thermal adsorption/desorption unit has been interfaced to the "cryogenic" system to conduct a direct comparison of the two preconcentration systems.

Results and Discussion

During the summer of 1988, air samples collected in stainless steel flasks at the Ministry's site at Dorset and other forested areas have been examined using the cryogenic preconcentration – GC analysis for C_2 and C_3-C_{10} hydrocarbons. Typically, 500 cm^3 of the air samples were sufficient for analysis of the natural NMHCs, e.g. ethylene, isoprene and terpenes, with a detection limit of <0.1 ppb volume mixing ratio. Possible deterioration of samples during storage was not apparent for light HCs up to a week after collection. Further tests on the sample integrity and preconcentration efficiency as well as performance optimization of the GC/MS system are in progress. Also, to enhance data acquisition speed and reproducibility, a fully automated cryogenic preconcentration system is being assembled.

References

1. Lusis, M.A. (1986) "Oxidant Control Strategy for Ontario: First Status Report", Ontario Ministry of the Environment internal report.
2. Kurtz, J. (Feb. 1987) "A Review of the Ontario Ozone Problem", Conference Proc. of North American Oxidant Symp. p.363.
3. Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H.H. Westberg, F.C. Fehsenfeld, (1987) "Models and Observations in the Impact of Natural Hydrocarbons on Rural Ozone", Nature, 329, 705-707.
5. Chameides, W.L., R.W. Lindsay, J. Richardson, and C.S. Kaing, (1988) "The Role of Biogenic Hydrocarbons in Urban Photochemical Smog: Atlanta as a Case Study", Science, 241, 1473-1475.
6. Kieser, B. (1988) "Development of a System for Sample Handling and Preconcentration in the Analysis of Ambient Air Samples for Trace Organic Compounds', Thesis, York University.
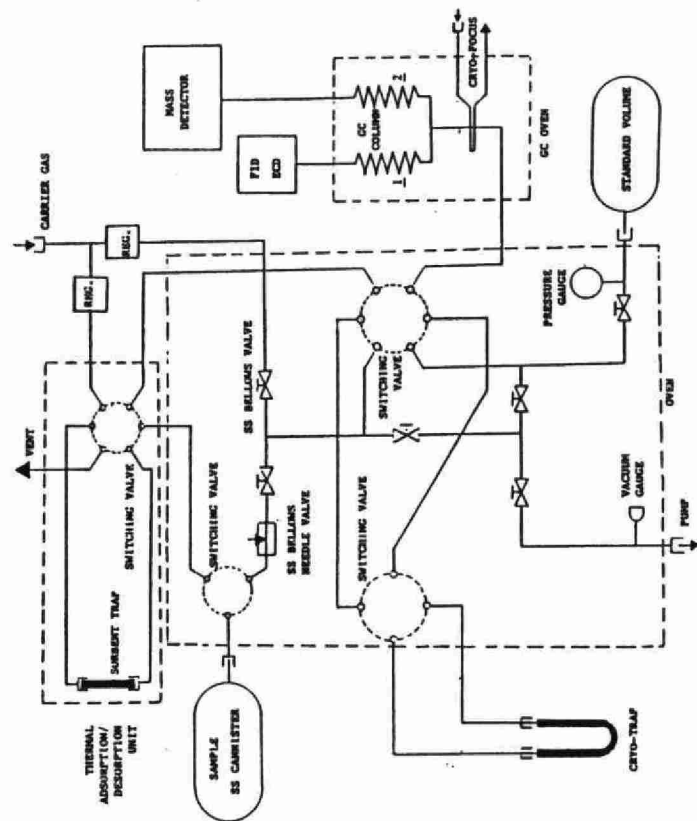
Fig.1: Schematic of Sample Preconcentration System for GC/MS Analysis

with monitoring plumes of a transborder origin. Many difficulties could be overcome if existing air pollution sampling networks, utilizing HiVol sampling equipment, could be simply and effectively adapted to collect airborne radionuclides.

For particulate radioactive contaminants, particulate filters already used in HiVol sampling networks are an effective sampling media. However, this media has no ability to trap gaseous radioiodines. Experience in the nuclear industry, and following the accidents at Three Mile Island and Chernobyl, demonstrate radioiodines are predominantly in the gaseous state. Experience has shown that molecular iodine (I_2) is the predominant species particularly in the initial release; however, organic iodides (mainly assumed to be CH_3I) can also form a significant fraction. As they are probably the most radiobiologically significant fission products, an effective monitoring program following a nuclear incident must have the ability to collect radioiodines, the most notable of which is ^{131}I. Several approaches are available to accomplish this. One method would be to deploy expensive portable high volume samplers using special deep-bed charcoal canisters. Another would be to design and manufacture deep-bed charcoal canisters which could be installed on the HiVol sampler. A third method, which requires no additional equipment purchase or modification, is the use of charcoal-loaded filter paper. Although having a lower collection efficiency for radioiodines, particularly organic iodides (methyl iodide), charcoal-loaded filter papers would be the easiest to deploy at a much lower cost.

3. CHARCOAL LOADED FILTER MEDIA SELECTION

Following an extensive literature and product search four suppliers of suitable charcoal-loaded filter paper were identified. From these suppliers eight media types were tested for radioiodine collection efficiency (retention). The suppliers and media types are shown in Table 1. The factors considered in selecting potential media included: the carbon loading of the media (g/m^2); the physical stability and durability of the charcoal/fibre matrix; and the addition of chemicals (KI, triethylenediamine) which enhance the collection of organic iodides. Table 2 shows the properties and specifications of the selected media.

Table 1. Charcoal-Loaded Filter Paper Suppliers

Supplier	Address	Media
Dexter Materials Division	Burlington, Ontario	Grade X3954
"	"	Grade 4703
F&J Specialty Products	Miami Springs, Flor.	CI 47
Whatman Paper Division	Clifton, New Jersey	Grade 72
Extraction Systems Inc.	Norwood, Mass.	Hyperm 16-2
"	"	Hyperm 7-5
"	"	Hyperm 12-5
"	"	Hyperm 13-2

Table 2. Charcoal-Loaded Filter Paper Specifications

Media	Carbon Loading (g/m^2)	Thickness (mm)	Chemical Impregnant
Grade X3954	106	0.84	None
Grade 4703	80	0.82	None
CI 47	n/a***	0.78	None
Grade 72	100	0.80	None
Hyperm 16-2*	540	3.5	TEDA**
Hyperm 7-5	240	1.2	TEDA
Hyperm 12-5	410	1.8	TEDA
Hyperm 13-2	440	2.5	TEDA

* The first number in the numerical coding for the Hyperm media represents the carbon loading in oz/yd^2, the second number represents the pressure drop in mm of water.
** TEDA - triethylenediamine at 5% of charcoal weight.
*** n/a - not available

4. EXPERIMENTAL DESIGN

Representative samples (approximately 50 mm diameter discs) of the charcoal-loaded filter media were tested for both molecular iodine (I_2) and methyl iodide (CH_3I) retention under controlled laboratory conditions. The filter media samples were sealed into P.V.C. envelopes with welded edges, in the center of which were cut 25 mm diameter holes to allow free passage of air through the center of the filters. The media samples were then clamped into test assemblies fabricated from standard 1" I.D. conical glass pipe. The P.V.C. envelopes provided a seal between the glass joints of the test assembly and the filter media, thus eliminating any inleakage of air. The test assemblies were equipped with a deep bed of high efficiency nuclear-grade charcoal downstream of the test media to trap all the iodine gas which passes the filter media.

The charcoal-loaded filter media and back-up charcoal were equilibrated with air at the test face velocity, relative humidity, and temperature for 30 minutes. The media was then challenged with an ^{131}I traced iodine (CH_3I or I_2) and humid air mixture (feed period) for 120 minutes. Following the feed period the charcoal-loaded filter media was purged with the humid air (elution period) for 30 minutes. The ^{131}I retained in both the charcoal-loaded filter media and back-up charcoal was determined using a specially calibrated NaI gamma spectrometry system. The percent retention of the charcoal-loaded filter paper was determined as follows:

$$R\ (\%) = C_F/(C_F + C_D) \cdot 100$$